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MULTIPLICITIES OF π-YLIDE GROUND STATES: COMPUTATIONAL EVIDENCE FOR A BREAKDOWN OF AROMATICITY ARGUMENTS

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AM1 and 3–21G computations, on the lowest singlet state of selected π-ylides, support the earlier conclusion that π-ylides are highly polar with highly reactive side-chains. The computations also indicate that the corresponding triplet states are lower in energy and have substantially reduced polarity. Contrary to the expectations derived from Hückel calculations, AM1 and 3–21G calculations suggest that the best π-ylide structures have non-aromatic rings. The heats of isomerization contradict earlier conclusions reached using topological resonance energies. π-Ylides are expected to afford different product structures depending on the electronic state of the π-ylide involved in a given cycloaddition reaction.

INTRODUCTION

A recent paper[1] suggests the possibility of a new subclass of very polar hydrocarbons, i.e. π-ylides. π-Ylides satisfy the definition of mesomeric betaines, viz. 'neutral conjugated molecules which can be represented only by dipolar structures in which both the positive and negative charges are delocalized within the π-electron system.[2] π-Ylides are even non-alterant substituted annulenes for which a Lewis structure containing two non-bonding electrons can be written. π-Ylides may be distinguished from structurally similar low-polarity non-alternant substituted annulenes by examining 'diradical' structures. When such a diradical structure is drawn with one endocyclic and one exocyclic electron, then that structure is a π-ylide if all ring π-bonds are endocyclic (Hückel results suggest that **1a** must be depicted as shown in **1b**), and it is a non π-ylide if any ring π-bond is exocyclic. The diradical representations for π-ylide structure **1a** and non-π-ylide structure **2** serve to illustrate these structural types (Figure 1).

A comparison of pairs of π-ylide and non π-ylide structural isomers[1] (e.g. **1b** and **3**) at the Hückel level indicated far more strongly polarized π-systems for the π-ylides. MNDO computations on the singlet states supported the Hückel view, assigning dipole moments of 6.99 and 1.63 D to **1b** and **3**, respectively.

Calculated topological resonance energies (TREs)[1,3] of π-ylides and their structural isomers led to the conclusion that π-ylides might well be accessible in the laboratory.

We have been concerned about the possibilities that (i) higher level MO computations might lead to decidedly less polar descriptions for hydrocarbon π-ylide singlets, (ii) a computational comparison of very polar singlets with triplets (which are expected to be much less polar) might reveal that hydrocarbon π-ylide triplets are the electronic ground states and (iii) if π-ylides are expected to be ground-state triplets, π-ylide cycloaddition reactions might be expected to give different products from those suggested previously[1] for the singlet states. Accordingly, we have done AM1 and 3–21G computations on the lowest singlet state of the π-ylides **1b**, **4** and **6** and the corresponding non π-ylides **3**, **5** and **7**. We have also carried out MNDO, AM1 and 3–21G computations on the lowest triplet state of each species.

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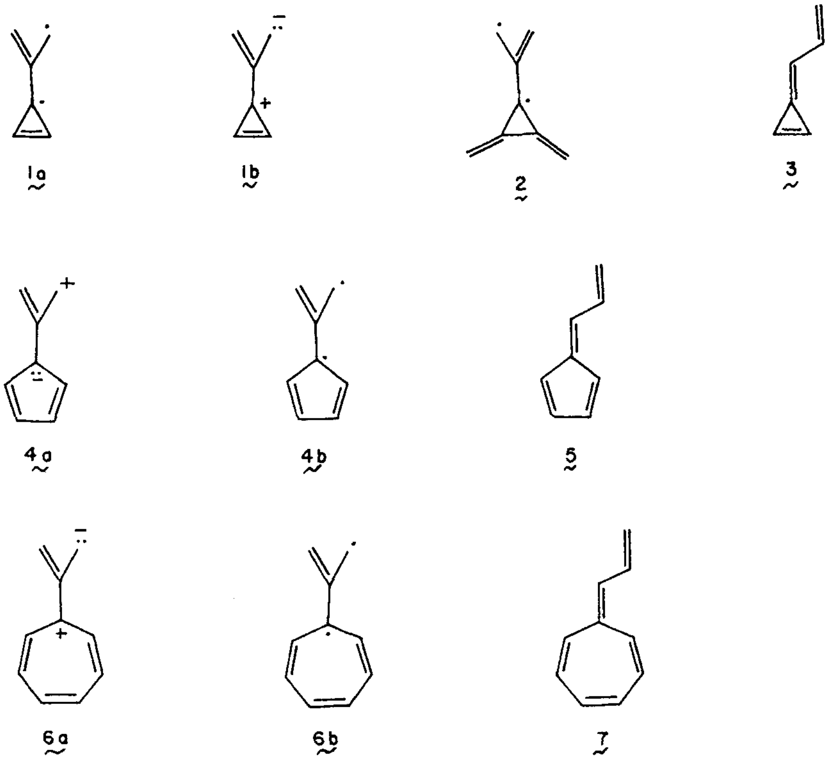


Figure 1. Structures of species **1–7**

METHOD

MNDO and AM1 computations were done using the MOPAC 5 program.[4] The 3–21G calculations were done using the GAUSSIAN 80 UCSF program[5] and the GAUSSIAN 86 program.[6]

The unrestricted Hartree–Fock (UHF) method was used for all triplet-state computations. Geometries were fully optimized subject to C_{2v} or C_s constraints as appropriate.

RESULTS

The MNDO, AM1 and 3–21G dipole moments for the lowest singlet state of the π-ylides and the corresponding non-π-ylide isomers are given in Table 1. All levels of theory indicate that π-ylides have much larger dipole moments than the non-π-ylide isomers. For species included here, the 3–21G method gives larger dipole moments than the semi-empirical methods. The 3–21G dipole moments of alkanes and alkenes are known to be in good agreement with experiment.[7]

Figure 2 gives the pertinent MNDO frontier orbitals for the π-ylides. AM1 orbitals are virtually identical with the MNDO orbitals and are not presented. The 3–21G and MNDO orbitals are not directly comparable owing to differences in basis sets and orthogonality assumptions. Nevertheless, analysis of the 3–21G frontier orbitals leads to the same conclusions reached earlier.[1] The side-chain is expected to be the site for reactions.

Table 2 lists the dipole moments for the lowest triplet state of the π-ylides and Table 3 gives calculated

Table 1. Calculated singlet-state dipole moments for π-ylides and selected structural relatives

	Dipole moment (D)[a]		
Compound	MNDO[1]	AM1	3–21G
1b	6·99	7·33	8·22
3	1·63	1·71	2·96
4a	7·37	7·82	9·35
5	1·05	1·09	1·08
6a	2·37	4·32	7·59
7	0·18	0·58	0·71

[a] For structures **1b**, **3**, **6a** and **7** the ring is electron deficient and for structures **4a** and **5** the ring is electron rich.

singlet – triplet energy differences. In each case, the lowest triplet state is calculated to be significantly lower in energy and significantly less polar than the singlet state. Structures **4** and **6** are predicted to be essentially non-polar in their lowest triplet states.

Figure 3 gives the 3–21G optimized geometries for the singlet and triplet states of the π-ylides **1b**, **4** and **6**. For each ylide, the ring C—C bond lengths show significantly less alteration in the singlet than in the triplet.

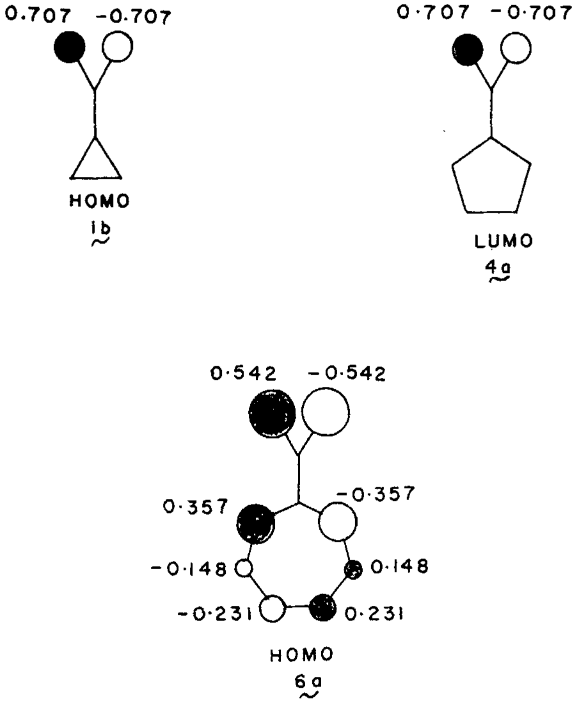


Figure 2. MNDO frontier orbitals for π-ylides

Table 2. Calculated triplet-state dipole moments for π-ylides

	Dipole moment (D)[a]		
Compound	MNDO	AM1	3–21G
1a	1·31	1·31	1·52
4b	0·10	0·27	0·07
6a	0·06	0·12	0·05

[a] For structure **1a**, the ring is slightly electron deficient.

Table 3. Calculated singlet–triplet energy differences for π-ylides

	$^1E - {}^3E$ (kcal mol^{-1})[a]		
Compound	MNDO	AM1	3–21G
1b, 1a	59	54	54
4a, 4b	62	53	63
6a, 6b	74	61	80

[a] 1 kcal = 4·184 kJ.

DISCUSSION

The Langler and Precedo description[1] of π-ylides is based on the Hückel approximation. Even though the Lewis structures for π-ylides must show two nonbonding electrons (these structures have been described as 'closed-shell biradicals'[8]), Hückel calculations do not show orbital degeneracy and Hückel atomic charges indicate surprising polarity.

TREs[1] indicate that π-ylides should be aromatic and more stable than their non-π-ylide isomers. These results are in accord with the Hückel $4n + 2$ aromaticity rule. For example, **1b** should be aromatic if two π-electrons were associated with the ring, making the ring electron deficient and the compound highly polar, whereas **4** should be aromatic if six π-electrons were associated with the ring, making the ring electron rich.

Higher level molecular orbital approximations, including *ab initio* 3–21G, applied to the lowest singlet state corroborate the Hückel result and the $4n + 2$ rule. The attribution of aromatic character to singlet π-ylides is supported as well by the optimized ring C—C bond lengths. Note also the MNDO, AM1 and 3–21G results are not significantly different from one another, except that 3–21G calculated dipole moments for singlet π-ylides are consistently higher than MNDO or AM1 dipole moments.

In the Hückel approximation, the lowest triplet state of a π-ylide would necessarily be an excited state since its molecular orbital configuration represents promotion of a HOMO electron to the LUMO. However, our results show that, in each case, the π-ylide ground state is a slightly polar or non-polar triplet, not the highly polar singlet. Evidently, the energies of the nonbonding HOMO and antibonding LUMO (or bonding HOMO and non-bonding LUMO) are close enough to make electron repulsion a critical factor in determining ground-state orbital configuration and, hence, multiplicity. In such a case, because Hückel π-energies do not account for electron repulsion, one would expect Hückel results and attendant aromaticity arguments to be unreliable.

Our earlier report[1] included TREs for π-ylides and their closely related structural isomers, e.g. **1b** and **3**. The TREs consistently implied greater stability and greater aromaticity for the π-ylides. Since the TREs were calculated for π-ylide singlets, we present, in Table

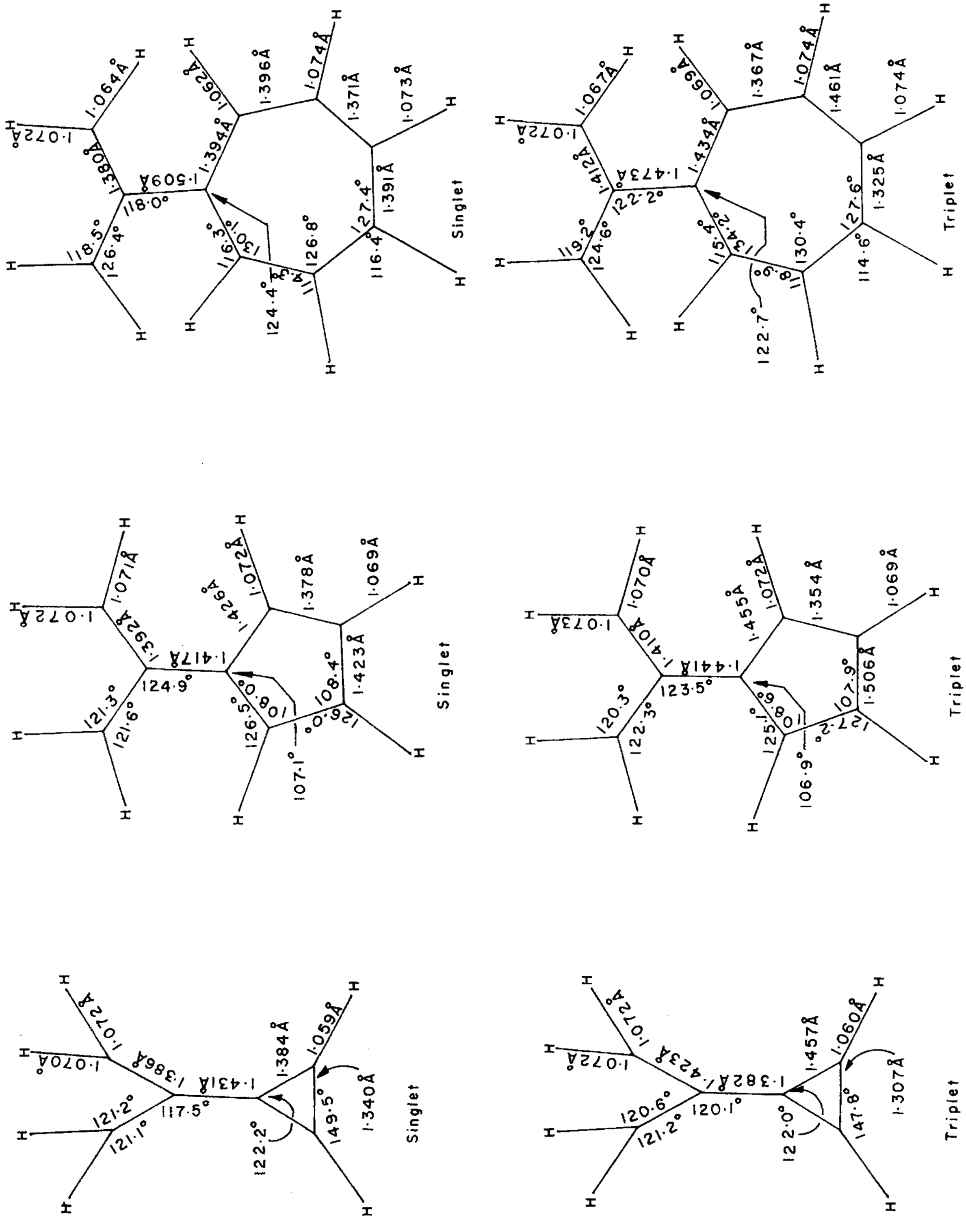
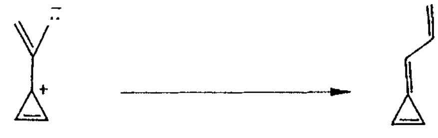


Figure 3. 3–21G optimized geometries for singlet and triplet π-ylides

4, a comparison of TREs (per electron) for isomeric pairs of singlet π-ylide and non-π-ylide hydrocarbons together with calculated heats of isomerization for the π-ylide to non-π-ylide isomerization illustrated in equation (1). The TRE values presented in Table 4 do not permit one to anticipate either the semi-empirical or the *ab initio* enthalpies of isomerization.



1b **3** (1)

In our earlier discussion of π-ylide singlets,[1] we presented a frontier orbital analysis for simple cycloaddition reactions, e.g. equation (2). In accord with the behaviour expected for **1b**, all of the π-ylides examined are expected to react exclusively in the side-chain.

1b (2)

To complement our earlier work, a frontier orbital analysis was carried out on the π-ylide triplets for the corresponding cycloaddition reactions (the present frontier orbital analysis was carried out using AM1 results). The C_6 π-ylide triplet **1a** will be used to illustrate the results obtained for all of the π-ylide triplets. Figure 4 presents the AM1 eigenfunctions for the two highest lying electrons of α spin (**1a** has 16 electrons of α spin and 14 electrons of β spin.)

The results in Figure 4 have two interesting implications: (i) one of the unpaired electrons is primarily associated with the ring and one primarily with the side-chain (we note that orbital spin populations lead to the same conclusion) and (ii) the more reactive site is the ring carbon bearing the substituent (SOMO 2, Figure 4).

Table 4. Topological resonance energies (per electron) and calculated heats of isomerization for the conversion of singlet π-ylides into non-π-ylides[a]

Compound	TRE (per electron)[b]	ΔH (isomerization) (kcal mol^{-1})[c] AM1	ΔH (isomerization) (kcal mol^{-1})[c] 3–21G
1b	0·078	−71	−75
3	0·016		
4a	0·036	−69	−87
5	0·005		
6a	0·021	−71	−83
7	0·001		

[a] Equation (1) presents a prototypical reaction.
[b] The unit for topological resonance energies is the Hückel β.
[c] 1 kcal = 4·184 kJ.

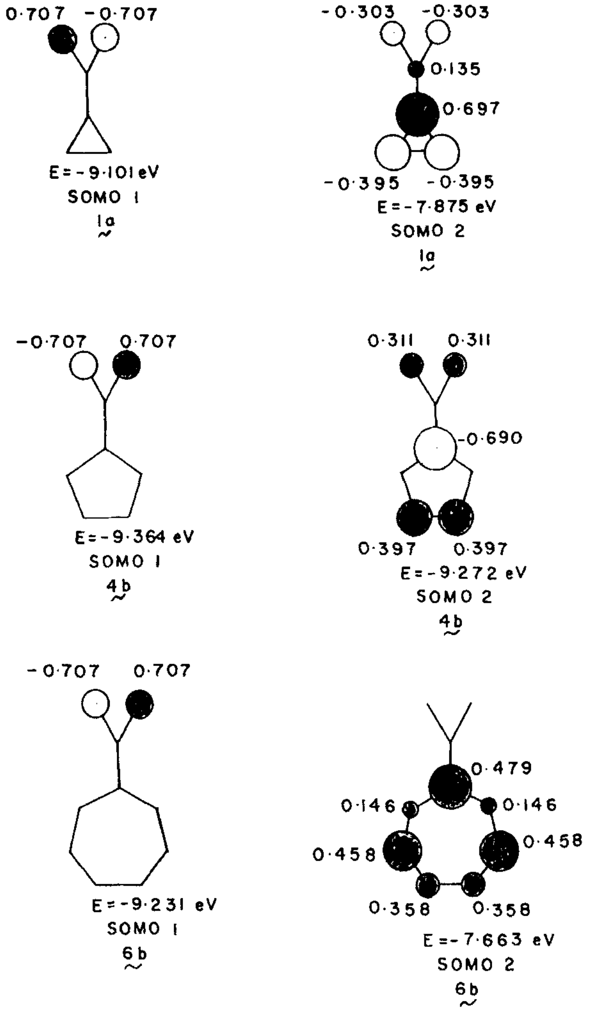
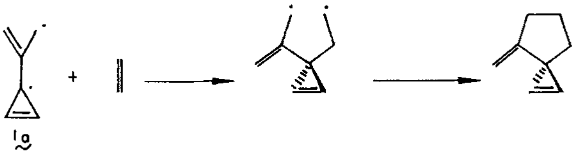
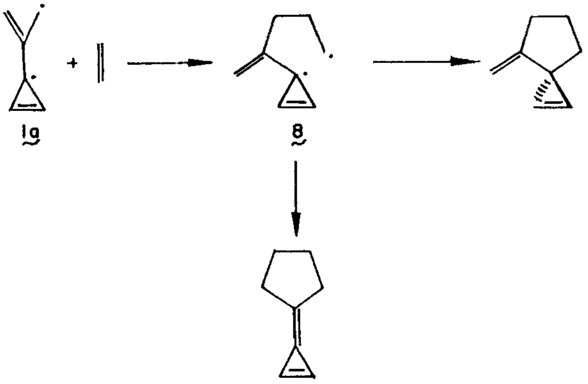


Figure 4. AM1 eigenfunctions for the two highest lying electrons of α spin

Assuming a stepwise process for π-ylide triplet cycloadditions, the mechanistic consequences of the foregoing results are portrayed in Scheme 1. Similar conclusions may be reached from the frontier orbitals for the other π-ylides examined (see Figure 4). (The eigenfunctions for electrons of α spin in **4b**, Ψ_{19}, Ψ_{20} and Ψ_{21}, are very nearly degenerate. Since the highest lying eigenfunction for β-electrons and Ψ_{21} contribute electron density to the same subset of atoms, Figure 4 presents Ψ_{19} and Ψ_{20} as the appropriate SOMOs for **4b**.) The ambiguity over which ring atom in **6b** would be



Scheme 1. Expected pathway for a π-ylide triplet cycloaddition based on a frontier-orbital analysis



Scheme 2. Expected pathways for a π-ylide triplet cycloaddition based on radical intermediate stability

preferentially involved in bond formation is partly ameliorated by orbital spin populations which clearly favour reaction at the ring carbon bearing the substituent.

In order to explore the possibility that radical reactions may proceed preferentially through the most stable radical intermediates, we have undertaken an examination of a series of monoradicals. The AM1 heats of formation of these radicals are reported in Figure 5. Judging from these results, it would seem that the most stable diradical intermediate obtained from any π-ylide triplet should result from bond formation to a side-chain terminus. As shown in Scheme 2, the intermediate diradical **8** would have more options for further reaction and should lead to a more complex array of products (cf Scheme 1). Hence the computational results permitted us to define three distinct outcomes for π-ylide cycloadditions, depending (i) whether the π-ylide is a triplet or a singlet and (ii) whether π-ylide triplet cycloadditions are frontier-orbital or intermediate-stability controlled. One can now hope to use the results of cycloaddition reactions as evidence for intermediate multiplicity in reactions which might go through π-ylides.

Our computational studies have important implications for any experimental programme intended to exploit π-ylides for the construction of cyclic compounds: (i) a hydrocarbon π-ylide is expected to be a ground-state triplet and therefore is likely to undergo cycloaddition reactions which give complex mixtures,

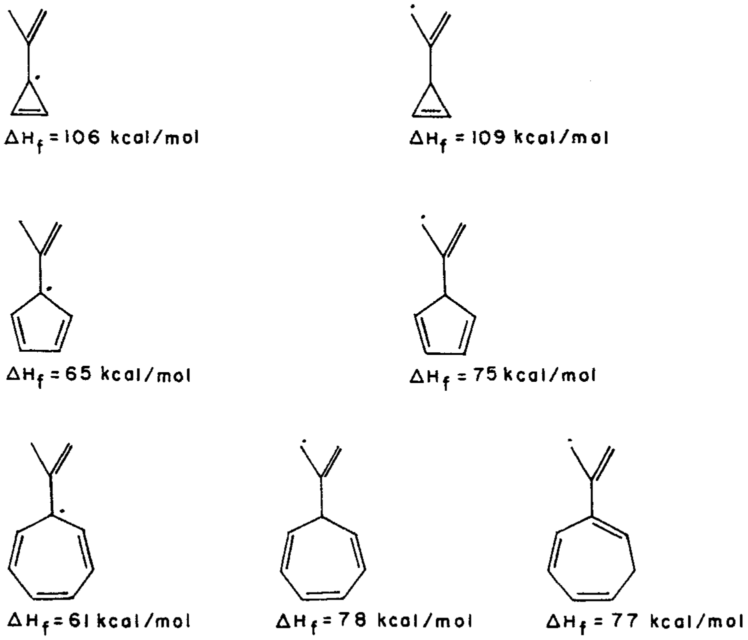


Figure 5. AM1 heats of formation for selected radicals

(ii) a high-polarity π-ylide singlet should undergo a cycloaddition reaction which would tend to give a single product [see equation (2)] but no hydrocarbon π-ylide singlet is likely to be accessible and (iii) future experimental and computational studies of π-ylides should be directed toward heteroatomic structures in the hope that they will have high-polarity singlet ground states which might be exploited for the construction of carbocycles and heterocycles.

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